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13. ABSTRACT (Maximum 200 words)

This ARO-sponsored research was concerned with performing some pioneering work on synthesizing titanium-titanium boride composite materials by in situ reaction processes, modeling and evaluating their mechanical behavior. The research has demonstrated that low cost in situ titanium matrix composites with titanium boride whiskers can be made with properties comparable to some high strength steels. The research also has demonstrated that novel titanium boride coatings can be engineered on to the surface of titanium. Further, functionally graded material architectures based on gradation of titanium versus titanium boride have been made with the idea of demonstrating the feasibility of making graded armor material for ballistic applications. Comprehensive investigations mechanical behavior of these composites were conducted. New approaches were used in fracture mechanical modeling of layered and graded materials. The over all research work was novel in each of the areas highlighted above and has resulted in new technologies and approaches in titanium composite material synthesis and mechanical behavior modeling.

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Microstructure and Mechanical Behavior of in-situ Ti-TiB whisker Composites

Final Progress Report (ARO Grant # DAAD19-99-1-0281)

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Foreword

This ARO-sponsored research was concerned with performing some pioneering work on synthesizing titanium-titanium boride composite materials by in situ reaction processes, modeling and evaluating their mechanical behavior. The research has demonstrated that low cost in situ titanium matrix composites with titanium boride whiskers can be made with properties comparable to some high strength steels. The research also has demonstrated that novel titanium boride coatings can be engineered on to the surface of titanium. Further, functionally graded material architectures based on gradation of titanium versus titanium boride have been made with the idea of demonstrating the feasibility of making graded armor material for ballistic applications. Comprehensive investigations mechanical behavior of these composites were conducted. New approaches were used in fracture mechanical modeling of layered and graded materials. The over all research work was novel in each of the areas highlighted above and has resulted in new technologies and approaches in titanium composite material synthesis and mechanical behavior modeling.

Statement of the Problem Studied

The ARO-supported research was aimed at making novel composite materials based on Titanium-Titanium Boride (Ti-TiB) architecture and studying their mechanical behavior. There were four distinct directions of the research: (i) Making of the in-situ titanium composites by growing TiB whiskers inside the titanium matrix in solid state, (ii) Growing TiB whiskers onto the surfaces of titanium to form a graded and wear resistant coating and (iii) Fabricating a functionally graded material armor plate with the proportion of Ti and TiB phases varying across the thickness of the plate and (iv) Performing fracture mechanical modeling of layered and graded materials to assist in the designing of Ti-TiB layered materials and graded structures. The research has met all the goals stated and the summary of research results are presented in the following in each section.

Summary of Most Important Results

(a) Synthesis of In-situ Titanium-Titanium Boride Composites

One aspect of the ARO supported research involved the in-situ synthesis of Titanium (Ti)-Titanium Boride (TiB) composites with β phase in the matrix by reaction sintering of TiB_2 with

Ti and alloying element powders. The goal was to examine the nature of TiB whisker formation in three different kinds of powder mixtures: (i) β-Ti alloy powders and TiB_2, (ii) α-Ti powder, a master alloy (Fe-Mo) powder containing the β−stabilizing elements and TiB_2, (iii) α-Ti powder, a β−stabilizing elemental powder (Mo or Nb) and TiB_2. The effects of powder packing and the relative locations of powder particles on the morphological changes in TiB whisker formation and their growth were studied at processing temperatures ranging from 1100^oC to 1300^oC. The morphology, size and the distribution of whiskers were found to be influenced by the powder packing conditions. A large particle size ratio in bimodally-packed mixtures led to the formation of TiB monolithic layer around β-grains. With a relatively finer starting powder, smaller size ratio and a trimodal packing arrangement, the TiB whiskers were found to be distributed more homogeneously in the matrix. The study also used the X-ray direct comparison method and the structure factor for the β-phase to determine the volume fraction of TiB phase from X-ray data. Tensile tests and fractographic investigations were carried out on selected composites. The evolution of composite microstructure, the influence of powder packing variables and the morphology and the growth of TiB whiskers and their effect on mechanical properties are discussed. This aspect of research has shown clearly that titanium composites containing TiB whiskers can be made easily and the microstructure and properties can be controlled. This research is comprehensively documented in publication 1.2.

(b) Synthesis of TiB whisker Coatings on Titanium Surfaces

One aspect of research involved examining the possibility of creating TiB whiskers on to the surface of titanium to produce a "functionally-graded coating". This study demonstrated the feasibility of synthesizing TiB whiskers on titanium (Ti) surfaces by solid state diffusion to form a hard and wear resistant coating. The microstructural and mechanical properties of the TiB coating layer have also been investigated. The TiB coating was formed by the solid-state diffusion of boron (B) from a powder mixture containing amorphous boron, Na_2CO_3 powder and charcoal (activated) powder. The diffusion process was carried out at various temperatures ranging from 800^0C to 1000^0C for various periods of time from 1 hr. to 24 hrs. The amount of Na_2CO_3 in the mixture was also varied. It has been found that extremely fine TiB whiskers form on the surfaces of titanium, with the whiskers growing more-or-less normal to the surface. A maximum coating thickness of about 218 μm was observed for the pack diffusion conditions at 850^0C for 24 hrs. with 15% Na_2CO_3. The kinetics of TiB formation was found to follow the growth rates in bulk composites. The XRD patterns of the coatings revealed the dominant TiB peaks with a very few TiB_2 peaks with negligible intensity at higher temperature and time. The surface hardness of the coated layer increased to a Vickers hardness of about 550 Kgf/mm^2 due to the presence of TiB whiskers in the coating. It was shown that pack diffusion of boron in solid state is a simple and very effective means of generating hard and wear resistant coatings on titanium. This research is comprehensively documented in publication 1.1.

(c) Synthesis and Modeling of Titanium-Titanium Boride Functionally Graded Materials

The another aspect of the ARO-sponsored study is the demonstration of an effective method to synthesize Titanium-Titanium boride (Ti-TiB) functionally graded materials (FGMs) tiles by exploiting the simultaneous TiB whisker formation in-situ and the densification occurring during the reaction sintering process. The macrostructure of the graded material was designed to have a beta-titanium (β-Ti) layer on one side with the composite layers of Ti-TiB mixture having increasing volume fraction of the TiB through the thickness. The approach utilized an optimized

tri-modal powder mixture consisting of α-Ti powder, a master alloy of the β–stabilizing-element powders (Fe-Mo) and TiB_2. The structure and properties of both of these FGMs were systematically characterized by X-ray diffraction, electron microscopy, and microhardness measurements. Interestingly, it has been found that two different kinds of TiB whisker morphologies were observed in the FGMs. The Ti-rich layers were found to have large and pristine TiB whiskers uniformly distributed in the Ti matrix. On the other hand, the TiB-rich layer was found to have a network of interconnected and relatively smaller TiB whiskers appearing as clusters. The layers of intermediate TiB volume fractions were found to consist of both the morphologies of TiB. The effectiveness of the X-ray direct comparison method for the determination of volume fractions of phases in the FGM layers was also demonstrated. Vickers microhardness level was found to increase dramatically from 420 kgf/mm^2 in the β-Ti layer to 1600 kgf/mm^2 in the TiB rich layer. The elastic residual stresses retained in the graded layers after fabrication were determined based on an elastic multilayer model. The nature of microstructure, the hardness variation and the distribution of residual stresses in these novel FGMs are discussed. This research is comprehensively documented in publication 1.3.

(d) Fracture Mechanics of Modeling of Layered and Graded Materials

The ARO-sponsored research also involved a fracture mechanics assessment of stress intensity factors in layered and graded materials, since there is no prior work in this area and additionally, this work was needed to enable the design of Titanium-Titanium Boride based layered and graded materials.

First, approximate stress intensity factor solutions for cracks in finite-width three layer laminates, with the crack located in the middle layer, were derived on the basis of force-balance between the applied stress and the modified Westergaard form of normal stress distribution ahead of the crack tip. This yielded a simple and closed form equation for the stress intensity factor that included the effects of the ratio of the moduli of the layers and the relative layer thicknesses. A comparison of the stress intensity factor values from this equation and with finite element data indicated that the difference between these two data sets was small for most of the crack lengths and the modulus ratio of the layers. The maximum difference occurred at crack lengths approaching the interface and at high moduli ratios, but was less than 10%, in general. The equations were also modified to incorporate the effects of residual stresses that arise during cooling after laminate processing, on the stress intensity factor. A comparison of the analytical data with the finite element data obtained by imposing thermal and mechanical boundary loads on the laminate specimens indicated a good agreement. The present closed form approximate solutions may be useful in fracture analyses of finite-width laminates containing cracks. This research is comprehensively documented in publication 1.4.

Secondly, a generalized method to determine the stress intensity factor equations for cracks in finite-width specimens of functionally graded materials (FGMs), based on force balance in regions ahead of the crack tip is provided. The method uses the Westergaard's stress distribution ahead of the crack in an infinite plate and is based on the requirement of isostrain deformation of layers of varying moduli ahead of the crack tip. It is shown that the modified Westergaard equation describes the normal stress distribution and the singular stress state ahead of the crack tip in a reasonably accurate manner. Based on this, closed-form analytical equations for the stress intensity factors of cracks in finite-width center cracked specimens were derived. Comparisons of the K values from the analytical equations with that obtained from FEM

simulations indicate that the derived stress intensity factor equations for FGMs are reasonably accurate. For the finite-width center-cracked-tension (CCT) specimen, the errors are less than 10% for most of the crack lengths for materials with the outer layer modulus ratios varying from 0.2 to 5. The stress intensity factors were found to be sensitive to the absolute values of moduli of the layers, the modulus ratio of the outer layers as well as the nature of gradation including the increasing and the decreasing functional forms. The stress intensity factor equations are convenient for engineering estimates of stress intensity factors as well as in the experimental determinations of fracture toughness of FGMs. This research is comprehensively documented in publication 1.6.

(d) Superplastic Deformation Behavior of Ti-TiB composites

This section presents the summary of work on superplastic deformation of Ti-TiB composites which is not published in any other form. In the ARO-sponsored research period, some mechanical testing, especially to evaluate the superplastic behavior of Ti-TiB composites were preformed. We summarize here the observations of superplastic behavior in the Ti-TiB composites, which is a very interesting phenomenon. As indicated in Figure 1, the load-displacement traces reveal considerable amount of superplasticity that is present in the Ti-TiB composites, with the 69% TiB sample showing the highest superplastic elongation. Figure 2 illustrates the deformed samples. The amount of superplastic elongation, measured as the net load line displacement, is plotted as a function of TiB volume fraction in Figure 3. It can be seen that the superplastic elongation is maximum, exceeding 200% for the Ti-69%TiB composite. Further analysis of this phenomenon is in progress. A manuscript, intended for publication in Scripta Materialia, is being prepared.
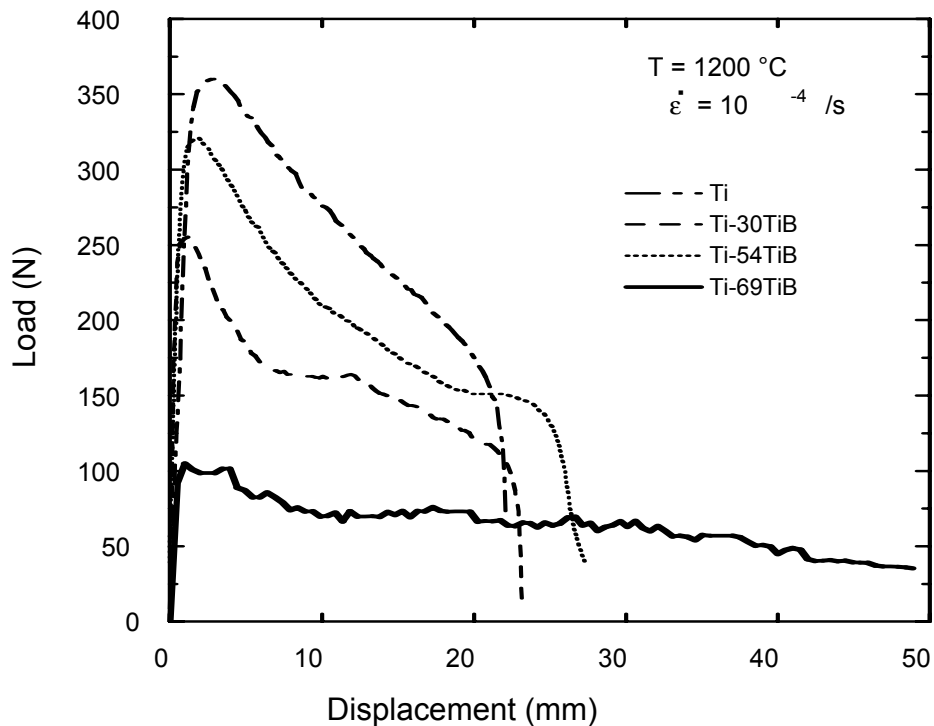

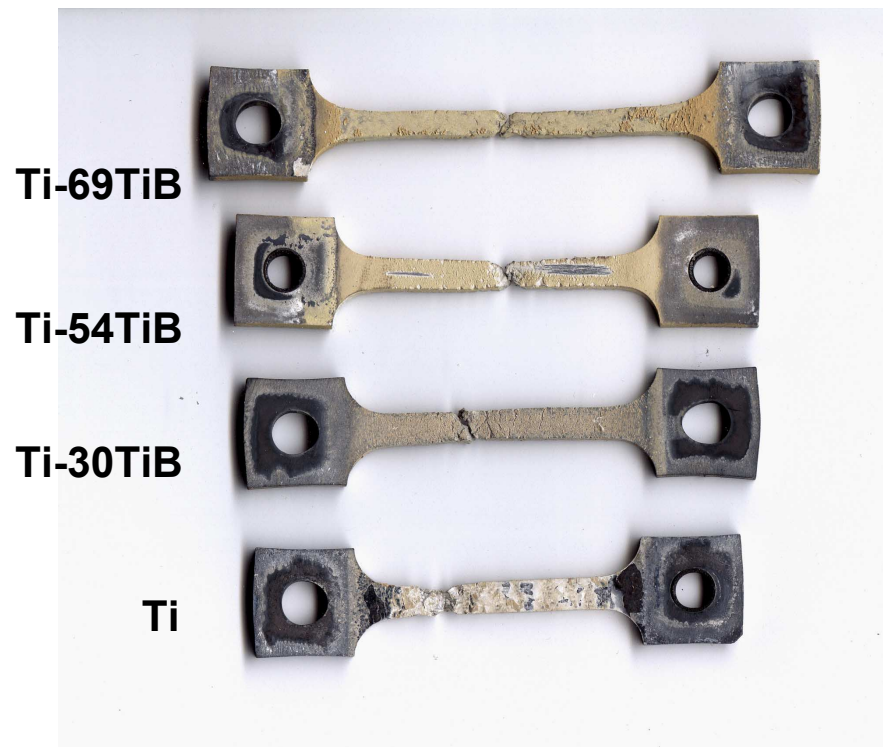Figure 1. Superplastic response of Ti-TiB composites

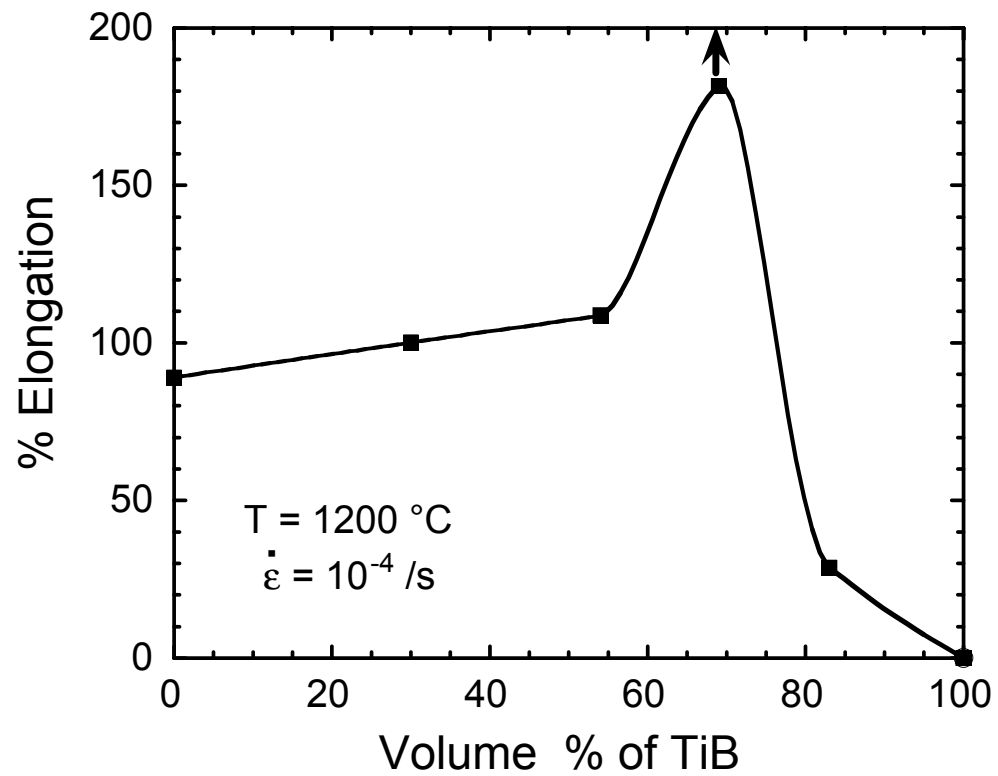Figure 2. Superplastically deformed Ti-TiB composites

Figure 3. The variation of superplastic elongation with the amount of TiB in the composite.

List of Publications

(a) Papers Published in peer-reviewed journals

1.1   S. Aich and K. S. Ravi Chandran, "Synthesis of TiB whiskers on Ti surfaces by solid state diffusion," **Metallurgical and Materials Transactions A**, Vol.33, No.11, November, 2002, p.3489-3498

1.2   K. Panda and K. S. Ravi Chandran, "In-situ synthesis of Ti-TiB composites with β-Ti matrix," **Metallurgical and Materials Transactions A**, Vol. 34A, No. 6, pp. 1371-1385, 2003

1.3   K. Panda and K. S. Ravi Chandran, "Titanium-Titanium Boride (Ti-TiB) Functionally Graded Materials Through Reaction Sintering: Synthesis, Microstructure and Properties," **Metallurgical and Materials Transactions A**, Vol. 34A, 2003, pp. 1993-2003

1.4   I. Barsoum and K. S. Ravi Chandran, "Approximate Stress Intensity Factors for a Crack in the Middle Layer of a Three Layer Laminate: A comparison of simple analytical solution with finite element calculations," **Engineering Fracture Mechanics**, Vol. 70, 2003, pp. 2015-2031

(b) Papers Published in non-peer-reviewed journals/conference proceedings

1.5   K. S. Ravi Chandran and K. Panda, "Discontinuously reinforced titanium composites with titanium boride whiskers on the horizon," **Advanced Materials & Processes**, Vol. 160, No. 10, October, 2002, p 59-62

1.6   K. S. Ravi Chandran and I. Barsoum, " Fracture Mechanics of Functionally Graded Materials (FGMs): Stress Intensity Factor Solutions and the Nature of Crack Arrest," **Mechanisms and Mechanics of Fracture: Proceedings of the Symposium in the Honor of Prof. J. F. Knott**, edited by W. O. Soboyejo, J. J. Lewandowski and R. O. Ritchie, TMS-AIME Publication, 2002, pp. 155-162

1.7   K. B. Panda and K. S. Ravi Chandran, "Synthesis of Ti-TiB Functionally Graded Materials by reaction sintering," **Proceedings of the 3rd International Conference on Functionally Graded Materials**, 6-7 May, Denver, CO, Metal Powder Industries Federation, NJ, compiled by R. G. Ford and R. H. Hershberger, Metal Powder Industries Federation, 2002, p. 34

(c) Papers Presented in Meetings but not published

1.8   K. S. Ravi Chandran, "Titanium-Titanium Boride Functionally Graded Materials," **Department of Metallurgy and Materials Science, Cambridge University**, UK., 30 May 2002 (invited presentation)

1.9   K. S. Ravi Chandran, "Insitu Titanium Metal Matrix Composites as Affordable Material Solutions, **Low Cost Titanium Workshop: Applications for Ship and Groud Vehicle Structures**, Baltimore, 10-11 December 2003 (invited presentation)

1.10   K. S. Ravi Chandran and K. Panda, "In-situ synthesis of Ti-TiB composites with β-Ti matrix," **Presented in Symposium on Structure and Properties of Titanium Alloys**, 2002 TMS Fall Meeting, October, Columbus OH

1.11   K. S. Ravi Chandran, "In-situ composites and functionally graded materials in the Ti-B system," **Special Seminar, Department of Materials Science and Engineering, University of Tennessee**, Knoxville, TN, June 2001 (Invited Presentation)

(d) Manuscripts in Preparation

1.12   S. Sahay and K. S. Ravi Chandran, "Superplasticity in Ti-TiB Composites," In preparation for submission to **Scripta Materialia**

1.13   K. S. Ravi Chandran, "Mechanical and Physical Properties of TiB," In preparation for Submission to **Journal of Materials Research**

Scientific Personnel Supported

Dr. K. S. Ravichandran,	Principal Investigator (Summer Salary)
Mr. Krutibas Panda	Graduate Research Assistant (MS, 2002, PhD 2003)
Mr. Imad Barsoum	Graduate Research Assistant (MS, 2002)
Ms. Shampa Aich	Graduate Research Assistant (MS, 2002)

Report of Inventions

An invention disclosure on the Synthesis of TiB whiskers on Ti surfaces for high performance coatings was filed with the University of Utah Technology Transfer Office in 2002.

Based on this disclosure, the University of Utah Technology Transfer Office has filed an International Patent Application entitled, **"Integral Titanium Boride Coatings on Titanium Surfaces And Associated Methods**," on 15 November 2003. (Inventors: K. S. Ravi Chandran and S. Aich)

Technology Transfer / Contact with ARL

The nature of ongoing project and the results obtained are communicated to Mr. B. A. Gooch, AMSRL-WT-TA, Army Research Laboratory, Aberdeen Proving Ground, MD, with respect to their implications for the development of Ti-TiB Functionally Graded Armor. We have sent five FGM plates, which are kind of prototypical armor plates, for initial ballistic testing at ARL. The results are awaited as there have been delays at the laboratory in scheduling the testing. Once preliminary results are known, this would help us to optimize the FGM plates further to enable better ballistic performance.